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A STUDY OF GAS GENERATORS FOR SHIP SALVAGE BUOYANCY SYSTEMS

by

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ABSTRACT. Gases and gas generating materials have been reviewed to determine which are most suitable for ship salvage buoyancy devices. Three missions have been considered: a 3,000-ton lift from an ocean depth of 850 ft and 75-ton lifts from 12,000 and 20,000 ft. Hydrogen, nitrogen, oxygen, methane, ethane, and ethylene are the only gases suitable for these missions even at 850 ft. Hydrogen, nitrogen, oxygen, and methane are useful at 12,000 and 20,000 ft, also. Cryogenic liquids offer the most economical source of buoyancy gases, but their application to the deeper missions may be restricted by the high-pressure storage problems associated with their development. The catalytic decomposition of hydrazine and the calcium hydride-seawater reaction are the most promising gas generating chemical reactions. Since the performance of the hydrazine decomposition has not been studied quantitatively at the high pressures encountered in the 12,000 and 20,000 ft missions, such an investigation must be conducted before this system can be evaluated with confidence.

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FOREWORD

This report presents the results of a survey of gases and gas generating propellants for ship salvage buoyancy devices. The investigation was initiated at the request of U. S. Civil Engineering Laboratory, Port Hueneme, California in February 1970 under Work Request WR-0-0079.

This report has been reviewed for technical accuracy by Dean H. Couch, Code 4584.

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INTRODUCTION

Buoyancy devices for ocean salvage are desirable because they make cumbersome connections to surface craft unnecessary. The objective of this survey is the identification and evaluation of buoyancy gases and gas generation methods for three lifting capabilities: 75 tons at 20,000 ft, 75 tons at 12,000 ft, and 3,000 tons at 850 ft. Gas generating methods and product gases are evaluated on the basis of cost, lifting efficiency, safety, and storage and handling characteristics.

SURVEY OF GASES

The number of gases which are useful as buoyancy media is quite limited especially for the deeper missions. Figure 1 shows a plot of the buoyancy factor[1] (pounds of water displaced/pound of gas) at 20,000 ft against molecular weight up to a molecular weight of 32. It is significant that this plot includes all the gases with densities less than that of nitrogen. Except for the trivial cases of rare isotopes (e.g., D_2, T_2, etc.) hydrogen, helium, methane, and neon are the only materials which are more buoyant than nitrogen.

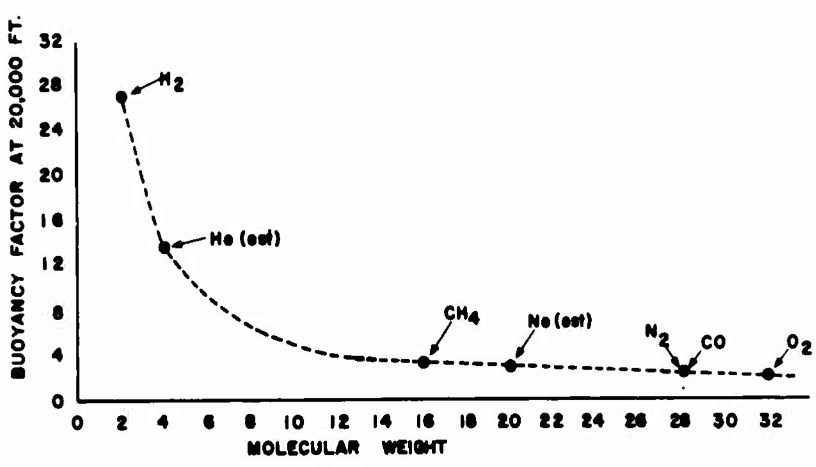

FIG. 1. Buoyancy of Gases at an Ocean Depth of 20,000 Feet.

[1] A sample buoyancy factor calculation is given in Appendix A.

The practical importance of the gas density is illustrated in Fig. 2 where the net buoyancy/weight of water displaced is plotted against the logarithm of the ocean depth. At depths of around 1,000 ft all the gas densities are quite small compared to water, and the net buoyancies of hydrogen and nitrogen are only slightly different. In the 10,000 to 20,000 ft region, however, the density of nitrogen approaches half that of water, and the net buoyancy is only about half that of hydrogen.

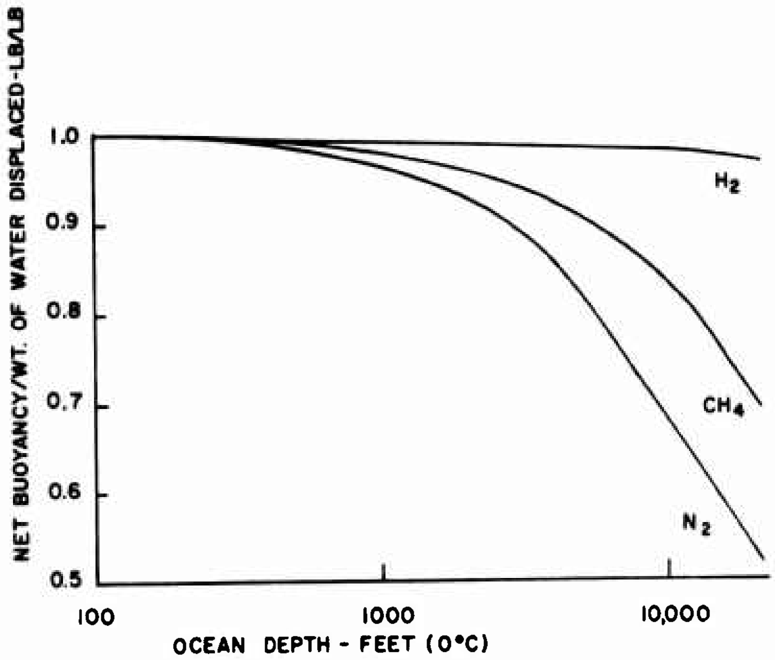

FIG. 2. Net Buoyancy of Hydrogen, Methane and Nitrogen.

In practical terms, the above considerations mean that, on the basis of gas density alone, roughly twice as many lifting pontoons would be required to raise a given object from 20,000 ft with nitrogen as with hydrogen. Nitrogen is clearly not attractive for the 12,000 and 20,000 ft applications if minimizing the size or number of the buoyancy devices is important.

If nitrogen is not useful at these depths; then what is? Referring again to Fig. 1 it is clear that only hydrogen and helium are significantly superior to nitrogen. Since helium cannot be generated chemically[2], only hydrogen remains. Thus, even though there are serious safety problems associated with its use (see Table 2b), hydrogen is most attractive as a buoyancy medium for deep ocean salvage.

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[2]Since the world's supply of helium is extremely limited, it is not practical for cryogenic applications on a large scale either.

At depths of less than 1,000 ft there are many gases which might be useful on the basis of density alone, but, here again, only hydrogen, helium, methane and neon are superior to nitrogen. Many gases can be rejected immediately on the basis of extreme toxicity (e.g., arsenic and selenium compounds) some (e.g., silanes, nitrogen-fluorine compounds) are very reactive, and others are quite dense (e.g., halogenated methanes, xenon). Gases which survive the toxicity[3], reactivity[4], and density[5], requirements are presented in Table 1 along with some of the problems associated with their use.

TABLE 1. Selected Properties of Buoyancy Gases

Gas	Mol. wt.	Boiling point (°C)	Comments
H_2	2.02	-252.8	Extremely flammable, high explosion hazard
N_2	28.02	-195.6	Non-toxic, inert
O_2	32.00	-183.0	Reactive with reducing agents
He	4.00	-268.9	Very limited supply
Ne	20.18	-245.9	Very limited supply
Ar	39.94	-185.7	Non-toxic, inert
Kr	83.8	-152.0	Fairly dense
N_2O	44.02	- 88.49	Moderate toxicity, moderate fire hazard, soluble in water
CO_2	44.01	- 78.2	Fairly dense, very soluble in water, low vapor pressure
CH_4	16.04	-161.5	Flammable
C_2H_4	28.05	-103.9	Flammable
C_2H_6	30.07	- 88.6	Flammable
Natural gas	.....	......	Flammable (85% CH_4, 10% C_2H_6 + C_3H_8 + N_2)

[3]The toxicity of a gas was considered unacceptable if it was rated as "high" in Ref. 1: i.e., "very short exposures to small quantities may cause death or permanent injury".

[4]The reactivity of a gas was considered excessive if it could not be expected to be stable under the environmental conditions anticipated for the buoyancy missions.

[5]Krypton is the densest gas included in Table 1.

It appears that H_2, N_2, O_2, CH_4, C_2H_4, C_2H_6, and natural gas are the only gases suitable for buoyancy even at the 850 ft depth.

GAS GENERATION

12,000, 20,000 FEET

The preceding discussion indicates that gas generating chemical reactions which are to be applied to buoyancy devices at depths in excess of 10,000 ft should produce gas containing a high percentage of hydrogen. At lesser depths greater amounts of heavier gases are acceptable. Two reactions which appear to offer the most promise for deep ocean buoyancy are the catalytic decomposition of hydrazine (N_2H_4) and the reaction of metal hydrides (LiH, CaH_2, etc.) with seawater. Certain reactive metals produce only hydrogen as a gaseous product and could conceivably be useful also. Recently, Pulsepower Systems, Inc. has suggested a non-hypergolic bipropellant (NHBP) gas generator employing the high-temperature, high-pressure, pulsed-mode reaction of JP-4 with red fuming nitric acid (RFNA). The system was presented as a low cost alternative to hydrazine applicable over the entire depth range of the ocean. The thermal decomposition of isopropyl nitrate and solid propellants have been considered also. The important characteristics and relative merits of these gas generating reactions are discussed below.

HYDRAZINE

Hydrazine (N_2H_4) has found extensive application in rocket and spacecraft propulsion, and the development of spontaneous catalysts for its decomposition has extended its utility to the production of gas for a variety of applications including underwater propulsion, underwater buoyancy, inflation of weather balloons, and positive expulsion of rocket fuels. Some important chemical and physical properties of hydrazine are given in Table 2, while the properties of the product gases, H_2, N_2, and NH_3, are summarized in Table 3.

The decomposition of hydrazine may be considered to take place in two steps:

$$N_2H_4 \longrightarrow 4/3NH_3 + 1/3\ N_2 \tag{1}$$

$$NH_3 \longrightarrow (1 - x)\ NH_3 + (x/2)\ N_2 + (3x/2)\ H_2 \tag{2}$$

The energy released from Reaction (1), which is exothermic, can be considered the driving force for the endothermic ammonia decomposition, Reaction (2)[6].

[6] The overall reaction is exothermic at all values of x at 25°C and atmospheric pressure.

TABLE 2. Selected Properties of Hydrazine (Ref. 1)

Molecular weight	32.05
Density	1.011 gm/cm^3 @ 15°C
Melting point	1.4°C;
Boiling point	113.5°C
Heat of formation, 25°C	12.05 kcal/mole (liquid)
Flash point	126°F (open cup); 100°F (anhydrous)
Low explosion limit	4.7% (anhydrous)
Upper explosion limit	100% (anhydrous)
Autoignition temperature	270°C
Toxicity	Toxic, may cause damage to liver and destruction of red blood cells. Can be via skin contact. Threshold limit value: 1 part per million in air, 1.3 mg/m^3 of air
Fire hazard	Moderate, when exposed to heat, flame, or reducing agents
Explosion hazard	Severe, when exposed to heat, flame or oxidizing agents
Fire fighting	Water, foam, mist, carbon dioxide, dry chemical or carbon tetrachloride
Cost and availability	Used extensively as a rocket fuel; available in large quantities $2.95/lb (Olin Corporation - 55 gal drums) $2.00/lb (Olin Corporation - tank cars, estimated) $1.42/lb (Current USAF price, April 1970)

TABLE 3. Selected Properties of H_2, N_2, and NH_3 (Ref. 1)

	H_2	N_2	NH_3
Molecular weight	2.02	28.02	17.03
Boiling point (°C)	-252.8	-195.6	-33.35
Gas density (gm/ℓ)	0.0899	1.2506	0.771
Lower explosion limit	4.1%	non-combustible	16%
Upper explosion limit	74.2%	non-combustible	25%
Autoignition temperature (°C)	585	non-combustible	651
Toxicity (threshold limit value)	non-toxic	non-toxic	50 ppm in air, 35 mg/m^3 in air

Figure 3 shows the adiabatic reaction temperature and product distribution as a function of the fraction (x) of the ammonia dissociated for a reaction pressure of 1,000 psig (Ref. 2). Clearly, the utility of hydrazine decomposition for generating buoyancy gases is very strongly dependent on the degree of ammonia dissociation[7].

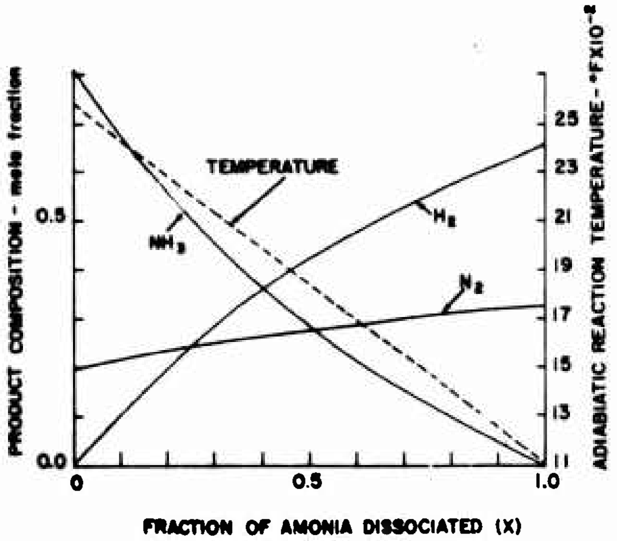

FIG. 3. Product Composition and Adiabatic Reaction Temperature for the Decomposition of Hydrazine at 1,000 psia.

What this means in practical terms is illustrated in Fig. 4, where the "buoyancy factor" (weight of water displaced/pound of reactant) is plotted as a function of the fraction of the ammonia decomposed (x) at an ocean depth of 20,000 ft. Values of x in excess of 0.8 are easily attainable at lower pressure, but no quantitative data exists for the high pressures (up to 9,000 psia) encountered at 12,000 to 20,000 ft depths although decomposition has been demonstrated qualitatively at pressures in excess of 11,000 psia at the Naval Weapons Center, China Lake. On purely equilibrium thermochemical grounds alone efficient (but somewhat reduced) ammonia decomposition is quite possible, but the effect of high pressure on the efficiency which is actually obtainable in practice is not known. A definitive quantitative investigation of the catalytic decomposition of hydrazine at high pressures is imperative before buoyancy systems can be designed with confidence. "Buoyancy factors" at 850, 12,000, and 20,000 ft are given in Table 4 for several values of x.

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[7]Since ammonia is the only toxic product (Table 3), the toxicity of the products is also reduced by efficient NH_3 decomposition.

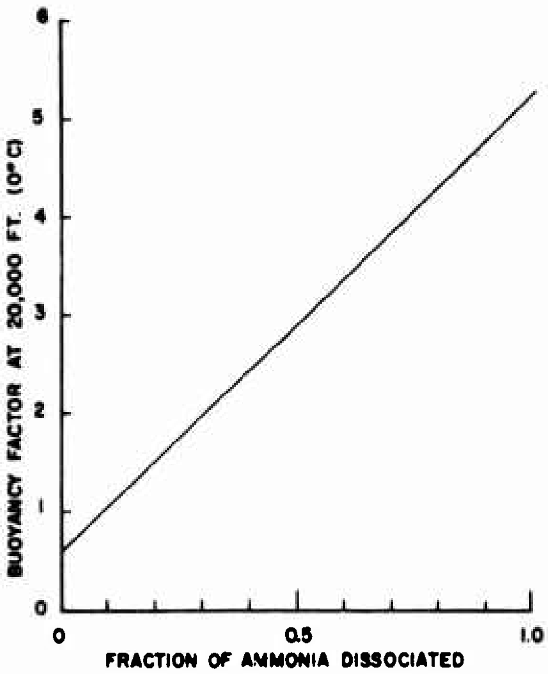

FIG. 4. Buoyancy Factor for Hydrazine vs. Fraction of Ammonia Dissociated at an Ocean Depth of 20,000 ft.

TABLE 4. Buoyancy Factors[a] for Hydrazine

Fraction of NH_3 Dissociated (x)	Buoyancy Factor		
	850 ft	12,000 ft	20,000 ft
1.0	81.43	7.41	5.25
0.8	66.93	6.09	4.32
0.5	45.17	4.11	2.93
0.2	23.43	2.12	1.54
0.0	8.90	0.80	0.61

[a]Buoyancy factor = weight of water displaced by gas/weight of fuel.

METAL HYDRIDES

The interaction of water with metal hydrides may be generalized by the following reaction:

$$MH_n + nH_2O \longrightarrow M(OH)_n + nH_2 \qquad (3)$$

where M designates the metal and n is the number of hydrogen atoms to which it is bound. The metal may be thought of as a carrier of hydrogen, and since half the hydrogen evolved is donated by the water, essentially twice as much gas is produced as for the equivalent metal - water reaction (see later). The fact that hydrogen is the only gaseous product is significant at the greater depths where the effect of gas density influences the net lift (see Fig. 2).

Metal hydrides are extremely reactive with water, and most ignite spontaneously in moist air. The ones of interest for gas generators are relatively non-toxic solids, but they produce hydrogen in the presence of heat or water, and fire fighting requires special dry chemicals.

Buoyancy factors for the metal hydrides, including some mixed hydrides[8], are given in Table 5. From a cost, stability (safety), and efficiency standpoint lithium hydride (LiH), calcium hydride (CaH_2), and "Hypron C"[9] are the most applicable to buoyancy devices. Calcium hydride (and probably "Hypron C") are considerably less reactive than lithium hydride and, consequently, offer some safety advantages.

A comparison of some pertinent properties of LiH, CaH_2, and "Hypron C" are given in Table 6. On the basis of cost and safety CaH_2 is to be preferred over LiH[10]. A cost evaluation of "Hypron C" is obscured by the processing and packaging expenses which are included in its price, but the actual fuel cost is probably similar to that of CaH_2.

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[8] The borohydrides and aluminum hydrides are quite expensive and are included here for the sake of completeness only. $NaBH_4$ with a $CoCl_2$ catalyst (Ventron Corporation) has been used as a hydrogen generator, but the cost is roughly twice that of LiH and CaH_2.

[9] The exact chemical composition of "Hypron C" is proprietary with Proteus, Inc., but its stated properties are very similar to those of CaH_2.

[10] $Ca(OH)_2$ is also considerably less caustic than LiOH.

TABLE 5. Buoyancy Factors of Metal Hydrides

Hydride	Buoyancy factor[a]		
	850 ft	12,000 ft	20,000 ft
LiH	110.14	10.09	6.87
NaH	36.47	3.34	2.28
KH	21.83	2.00	1.36
RbH	10.13	0.93	0.63
CaH	6.54	0.60	0.41
BeH_2[b]	158.80	14.55	9.91
MgH_2	66.51	6.09	4.15
CaH_2	41.60	3.81	2.60
SrH_2	10.92	1.81	1.23
BaH_2	12.66	1.16	0.79
AlH_3	87.56	8.02	5.46
"Hypron C"	40.38	3.70	2.52
$LiBH_4$	160.79	14.73	10.03
$NaBH_4$	92.58	8.48	5.78
KBH_4	64.93	5.95	4.05
$LiAlH_4$	92.28	8.45	5.76
$NaAlH_4$	64.86	5.94	4.05
$KAlH_4$	49.95	4.58	3.12

[a] Buoyancy factor = weight of water displaced by gas/weight of fuel.

[b] Beryllium compounds are extremely toxic.

TABLE 6. Selected Properties of Lithium Hydride, Calcium Hydride, and Hypron C

Property	LiH	CaH_2	"Hypron C"
Molecular wt.	7.95	42.10	....
Melting point	680°C	600°C	....
Density	0.82 g/cm^3	1.8 - 1.9 g/cm^3	1.69 g/cm^3
Heat of formation	-21.34 kcal/mole	-46.6 kcal/mole	....
Toxicity	Low	Low	Low
Fire hazard	High in presence of heat or water	High in presence of heat or water	High in presence of heat or water
Explosion hazard	High in presence of heat or water	High in presence of heat or water	High in presence of heat or water
Fire fighting	Requires special dry chemicals	Requires special dry chemicals	Requires special dry chemicals
Cost and availability[e]	$7.90/lb[a] 8.15/lb[b]	$2.90/lb[c]	$4.95/lb[d]
Buoyancy cost $/lb at 20,000 ft	1.15	1.11	1.92[d]

[a]10,000 lb lots, Lithium Corporation of America.

[b]1,000 lb lots, Lithium Corporation of America.

[c]25 lb lots, Ventron Corporation - 95% (1-inch lumps) to 93% (-40 mesh) pure.

[d]Proteus, Inc., includes the cost of processing and packaging into sealed cartridges.

[e]All these hydrides are available in quantities sufficient for these buoyancy applications.

METALS

Many metallic elements react with water to produce hydrogen gas and a metal hydroxide:

$$M + nH_2O \longrightarrow M(OH)_n + n/2\ H_2$$

where n is an integer (1,2,3) equal to the "valency" of the metal. Buoyancy factors for several water-reactive metals are given in Table 7.

TABLE 7. Buoyancy Factors of Water Reactive Metals.

Metal	Buoyancy factor[a]		
	850 ft	12,000 ft	20,000 ft
Li	63.09	5.78	3.94
Na	19.04	1.74	1.19
K	11.20	1.03	0.70
Mg	36.02	3.30	2.25
Al	48.68	4.46	3.04

[a]Buoyancy factor = weight of water displaced by gas/weight of fuel.

Magnesium and aluminum are attractive from a cost standpoint, but their reaction with water is slow due to the formation of a passivating oxide layer. Lithium, sodium, and potassium are extremely reactive with water and are usually stored in oil for protection from atmospheric moisture. Sodium and potassium are extremely inefficient on either a weight or volume basis. For example, in order to fill a lifting pontoon with hydrogen at 20,000 ft using the sodium-seawater reaction, a volume of solid sodium equivalent to almost 90% of the volume of the pontoon would be required. Lithium is not competitive economically (Table 8).

JP-4/NITRIC ACID

Recently, Pulsepower Systems, Inc., has proposed the development of a gas generating system based on the high-temperature, high-pressure (50,000 - 60,000 psia), pulsed-mode reaction of JP-4 (jet aircraft fuel) and red fuming nitric acid (RFNA). The operating principle involves injecting the two reactants into a chamber (much like a gun chamber) where they are mixed, ignited and reacted, and allowed to expand rapidly into a relatively low-pressure (up to 9,000 psia) environment. The process would then be repeated many times in a manner similar to the operation of an automatic rifle. The utility of this device depends upon the "freezing" of the high-pressure, high-temperature product gas composition during expansion since the low-temperature equilibrium products would be useless as a buoyancy medium.

TABLE 8. Selected Properties of Lithium and Sodium

Property	Lithium	Sodium
Atomic weight	6.94	23.0
Density (gm/cm^3)	0.534 @ 25°C	0.9710 @ 20°C
Melting point (°C)	179	97.81
Boiling point (°C)	1317	892
Autoignition temperature in air (°C)	180	115
Toxicity	Caustic Li_2O or LiOH formed with heat or water	Caustic NaOH formed with moisture
Fire hazard	High in presence of heat, water, acids, oxidizers	High in presence of heat, water, acids, oxidizers
Explosion hazard	High, produces H_2 with moisture	High, produces H_2 with moisture
Fire fighting	Special mixtures of dry chemical, soda ash, graphite	Soda ash, dry NaCl, graphite in order of preference
Cost and availability[a]	\$8.00/lb[b]	\$0.30/lb[c]

[a]Both sodium and lithium are produced in quantities sufficient for these buoyancy missions.

[b]Foote Mineral Company, Exton, Pennsylvania; 1,000 lb or more; 1/4 to 2 lb ingots.

[c]U. S. I. Chemicals, New York; 14,500 lb lots; 5, 12 lb bricks.

Table 9 (provided by Pulsepower) contains "buoyancy factor" and cost comparisons for JP-4/RFNA, hydrazine, and liquid nitrogen at ocean depths of 850, 2,800, and 20,000 ft. The calculated high-pressure, high-temperature product composition for an oxidizer/fuel ratio of 2.2 is given in Table 10.

If the system could be made to work, it would offer an order of magnitude advantage in cost over other methods of generating buoyancy by chemical reaction (on a simple cost of propellant per weight of water displaced basis). However, the effective density of the predicted gaseous products is only slightly less than the density of nitrogen, and roughly twice the displacement would be needed to lift a given load from 20,000 ft as would be required with an equal volume of hydrogen (see Fig. 2). At lesser depths, where cryogenic liquids (e.g., N_2) may be applied, JP-4/RFNA is not competitive economically (Table 9).

TABLE 9. Buoyancy Factor and Unit Lift Cost of JP-4/RFNA, N_2H_4, and LN_2 at 0°C (Pulsepower Systems, Inc.)

Operating depth, 0°C	JP-4/RFNA		Hydrazine		Liquid Nitrogen (LN_2)	
	Buoyancy factor	Lift cost[a] ($/lb lift)	Buoyancy[d] factor	Lift cost[b] ($/lb lift)	Buoyancy factor	Lift cost[c] ($/lb lift)
20,000 ft (605 atm)	2.32[e]	0.039	4.32	0.33	.....	.....
2,800 ft (85.5 atm)	12.3[e]	0.0073	23.8	0.06	.....	.....
850 ft (26.7 atm)	37.2	0.00242	72.0	0.0197	35.0	0.00107

[a]Based on a propellant cost of $0.09/lb.

[b]Based on a propellant cost of $1.42/lb.

[c]Based on a propellant cost of $0.037/lb.

[d]80% NH_3 dissociation.

[e]These values are approximately 5% too high because NH_3 and CO_2 have been considered gases while they are, in fact, condensed at these pressures. NH_3 is condensed at 850 ft also.

TABLE 10. High-Pressure, High-Temperature Product Gas Composition from the Reaction of JP-4 with Red-Fuming Nitric Acid (Pulsepower Systems, Inc.)

Propellant gas	Moles[a]
CO	1.813
CO_2	0.266
H_2	1.395
CH_4	0.160
H_2O	0.893
NH_3	0.018
N_2	0.556

[a]Reactants: RFNA: 68.75 gms, JP-4: 31.25 gms.

Some properties of JP-4 and RFNA are given in Table 11. JP-4 is flammable, and RFNA is very corrosive and quite toxic. Handling problems would be at least as great as with hydrazine.

TABLE 11. Selected Properties of JP-4 and Red-Fuming Nitric Acid.

Property	JP-4	RFNA
Boiling point	....	86°C (HNO_3)
Specific gravity	0.751 - 0.802	1.564 - 1.575
Flash point	-23 to 1°C	....
Autoignition temp.	468°F	....
Threshold limit value	....	2 ppm in air

It should be pointed out that this system is only a concept, and development time, costs, and actual performance are not certain. The large propellant cost advantage must also be weighed against the high gas density (low net buoyancy) for the deeper missions.

ISOPROPYL NITRATE

It has been suggested (Ref. 8) that isopropyl nitrate ($i - C_3H_7NO_3$) will decompose under ideal conditions to give a quantitative yield of hydrogen, nitrogen, and carbon monoxide (a useful gas mixture for underwater buoyancy):

$$i - C_3H_7NO_3 \longrightarrow 3CO + 1/2\ N_2 + 7/2\ H_2 \qquad (5)$$

Since it was suspected that this ideal product distribution was unlikely, a computer calculation[11] was performed to determine the actual theoretical product distribution allowed by chemical thermodynamics. The results of these calculations, which are summarized in Table 12 for the ocean depths of interest, reveal that Reaction 5 is indeed an oversimplification. The calculated product distribution results in much lower buoyant efficiencies, and the mixture is toxic (NH_3, CO, HCN), flammable (H_2, C, CH_4, NH_3, CO, HCN), and includes solid material (C), which would foul the catalytic reactor proposed in Ref. 8.

TABLE 12. Thermodynamic Equilibrium Product Distributions for the Decomposition of Iospropyl Nitrate at Ocean Depths of 850, 12,000, and 20,000 Ft.

Product	Moles of product[a]/100 gms of $i - C_3H_7NO_3$		
	850 ft	12,000 ft	20,000 ft
H_2	2.3857	1.6816	1.5312
C[b]	0.2653	0.1398	0.1174
CH_4	0.2923	0.5738	0.6333
NH_3[c]	0.0018	0.0071	0.0090
H_2	0.3570	0.4886	0.5163
N_2	0.4747	0.4717	0.4705
CO[c]	2.0957	1.9114	1.8631
CO_2	0.2009	0.2271	0.2374
HCN[c]	......	0.0011	0.0015

[a]Products less than 0.001 moles have not been included.

[b]Solid carbon.

[c]Toxic.

[11]Calculations performed by D. R. Cruise, Analysis Branch (Code 4535) Naval Weapons Center, China Lake, California.

Some pertinent properties of isopropyl nitrate, including the maximum buoyancy factors allowed, are given in Table 13. These buoyancies are the maximum possible assuming 100% reaction efficiency; it is quite probable that, especially at the higher pressures, much lower efficiencies would be obtained. Isopropyl nitrate does not appear attractive for underwater buoyancy applications.

TABLE 13. Selected Properties of Isopropyl Nitrate.

Molecular weight	1.05
Density	1.036 gms/cm^3 @ 19°C
Heat of formation	-45.7 kcal/mole (gas); -55.55 kcal/mole (liquid)
Boiling point	102°C
Toxicity	Slightly toxic
Fire hazard	High when exposed to heat or flame
Explosion hazard	Sensitive to mechanical shock; may explode on heating
Fire fighting	Alcohol foam
Buoyancy factors	850 ft: 46.89 lb lift/lb propellant 12,000 ft: 3.51 lb lift/lb propellant 20,000 ft: 2.57 lb lift/lb propellant
Apparent molecular weight of product gases at 0°C	850 ft: 16.56 12,000 ft: 17.11 20,000 ft: 17.46
Adiabatic reaction temperature	850 ft: 975°C 12,000 ft: 1192°C 20,000 ft: 1241°C

SOLID PROPELLANTS

Solid propellant gas generators have found extensive application in rocket technology and have been reviewed as possible sources of underwater buoyancy gases (Ref. 9-10). They have not been considered competitive[12] for the following reasons:

1. The extreme difficulty with which reaction rate control and stop and restart capability can be obtained.

2. The exponential increase of the reaction rate with increasing pressure, i.e., a strong dependence of the gas evolution rate on ocean depth.

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[12] Except for the water-reactive materials already discussed.

3. The presence of solids in the reaction products

4. The very low efficiencies possible.

In order to obtain an estimate of the efficiency of solid propellant gas generators, a computer calculation[13] was performed on a typical fuel[14] (composition classified) at 10,000 psi. The gaseous products were composed predominantly of H_2O, CO, CO_2, N_2, H_2, and CH_4, and the buoyancy factor at 20,000 ft was less than 2.0 even assuming 100% reaction efficiency. It is believed, in agreement with Ref. 9-10, that solid propellants are not promising candidates for buoyancy gas generators.

850 FEET

Of course all the gas generating methods discussed for the deep missions are applicable to lesser depths also. However, at depths of less than 1,000 ft, where the gas density is not so critical a factor, their relative merits are altered somewhat; e.g., nitrogen becomes almost as useful as hydrogen. Moreover, cryogenic liquids become attractive alternatives to chemical reactions and are, in fact, more economical.

LIQUID HYDROGEN

Liquid hydrogen (Table 14) is used extensively as a fuel in the space program and is available in large quantities. It has the highest buoyancy of any gas, and its price is competitive with that of liquid nitrogen. There are two serious problems associated with its application to underwater buoyancy, however. It has an extremely low storage temperature (boiling point = -252.8°C), which results in a very rapid boil-off rate compared to nitrogen or natural gas. This could be a serious handicap if the liquid must be stored for some time before deployment of the buoyancy device. Storage of liquid hydrogen in large quantities on the surface is an accomplished fact, but providing adequate insulation for storage during the actual submerged operation could be a very serious problem indeed.

The second problem is the extreme flammability of the gaseous hydrogen. Hydrogen-air mixtures are detonable at concentrations of from 4.1 to 74.2% of hydrogen whereas natural gas (methane) has a much lower explosive range of from 5.3 to 14%, and nitrogen is non-combustible (Table 10).

LIQUID NITROGEN

Some pertinent properties of nitrogen are shown in Table 14. It is readily available as a cryogenic liquid and could, in principle, be

[13] Calculations performed by J. Smith, Engineering Projects Branch (Code 4574), Naval Weapons Center, China Lake, California.

[14] The cost of this fuel is approximately $7.50/lb.

condensed from the atmosphere on board ship (in fact, unseparated liquid air would be equally as useful at 850 ft, and its use would obviate the need for fractionation equipment to remove the oxygen). Its low cost ($0.037/lb) makes it a leading contender for lifting large objects from moderate depths.

TABLE 14. Selected Properties of Cryogenic Hydrogen, Nitrogen and Liquid Natural Gas

Property	Hydrogen	Nitrogen[a]	Natural Gas[b] (methane)
Molecular weight	2.02	28.02	16.04
Boiling point (°C)	-252.8	-195.8	-161.5
Density (gm/cm^3) liquid	0.070 (-252°C)	0.808 (-195.8°C)	0.415 (-164°C)
Upper explosion limit (gas)	74.2%	Non-combustible	14%
Lower explosion limit (gas)	4.1%	Non-combustible	5.3%
Autoignition temperature (°C)	585	Non-combustible	538
Toxicity	Non-toxic	Non-toxic	Non-toxic
Fire hazard	Very high	Non-toxic	High
Explosion hazard	Very high	Non-combustible	High[c]
Fire fighting	CO_2 or dry chemical	Non-combustible	CO_2 or dry chemical
Cost ($/lb)	0.162[d]	0.037[e]	0.0012 - 0.0030 (Ref. 4)

[a]The properties of liquid air are very similar to those for nitrogen and are not listed separately.

[b]A nominal composition for natural gas (Ref. 1) is 85% methane, 10% ethane + propane, butane, and nitrogen. The properties listed here are those of pure methane.

[c]Although there is a significant explosion hazard associated with the use of natural gas, it is much less than for hydrogen (see explosion limits given above).

[d]F.o.b. Linde Corporation, Ontario, California in 7,200 lb dewar trailers. Transportation costs are approximately $0.50/mile.

[e]Airco, Vancouver, Washington. $0.032/lb f.o.b. the factory plus a typical trip cost of $175 for a 35,000 lb load delivered to the Navy at Bremerton, Washington.

LIQUID NATURAL GAS

Also included in Table 14 are data on natural gas. Shortages in domestic natural gas supplies have prompted preparations for the importation of large quantities of liquid natural gas (LNG) by tanker from Algeria, Venezuela, Canada, and possibly Alaska (Ref. 4). LNG is already transported on a regular basis from Nikiski, Alaska to Tokyo.

Natural gas is about 85% methane, is a more efficient buoyancy medium than nitrogen, and LNG is at least an order of magnitude cheaper than LN_2. LNG has the advantages of a higher cryogenic storage temperature, but nitrogen is essentially inert while LNG is combustible. Since LNG is already being transported by ship, it appears that the safety hazards are not insurmountable.

SUMMARY AND COMPARISON

COST AND AVAILABILITY

Table 15 shows the expected propellant cost of generating 3,000 tons of net buoyancy at 850 ft and 75 tons of buoyancy at 12,000 and 20,000 ft. It has been assumed that condensed reaction products (e.g., NH_3 in the hydrazine system and $Ca(OH)_2$ in the calcium hydride reaction) are expelled and, therefore, do not contribute to the load. The buoyant gas, however, must be lifted and has been subtracted from the gross buoyancy (weight of water displaced).

The price of hydrazine has been assigned two values: $1.42/lb, the current USAF price, and $2.95/lb, the current commercial price (Olin Corporation - 55 gallon drums). It is believed that the higher price is more useful for comparison with the metal hydrides since the quotations for the latter are commercial, not government contract, prices. Even on this basis hydrazine appears more economical provided, of course, that high ammonia dissociation levels are obtained[15].

For the 850 ft mission, where handling of cryogenic liquids is more convenient and gas density is not so important, liquid nitrogen (LN_2) (Ref. 3) and liquid natural gas (LNG) (Ref. 4) offer dramatic reductions in propellant cost. It seems safe to assume that the cost of LN_2 or LNG would be a negligible fraction of the total expense of any large salvage operation[16]. The storage and handling problems associated with liquid hydrogen weigh heavily against its use.

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[15] If the ammonia dissociation efficiency drops below 50%, the hydrides become more economical (see Fig. 4).

[16] Transportation costs can be a significant fraction of the cost of cryogenic liquids (approximately $0.50/mile for 7,200 dewar trailers of liquid hydrogen).

TABLE 15. Propellant Costs for Deep Ocean Buoyancy[a]

System	Propellant Cost ($)[a]		
	3,000 tons[b]	75 tons[b]	
	850 ft	12,000 ft	20,000 ft
N_2H_4[c] ($1.42/lb)	129,000	41,000	61,000
N_2H_4[c] ($2.95/lb)	268,000	85,000	128,000
Na	47,400	13,240	19,660
LiH	429,000	119,000	176,000
CaH_2	419,000	116,000	171,000
"Hypron C"[d]	715,000	198,000	292,000
LH_2	2,200	626	931
LN_2	7,000	2,000	2,600
LNG (CH_4)	132	35	55
JP-4/RFNA (100% efficiency)	18,000	6,000	10,000

[a]Solid propellants and isopropyl nitrate have not been included as they are not considered competitive for reasons other than cost.

[b]It is assumed that solid or liquid reaction products are expelled and do not, therefore, contribute to the load. The weight of the buoyant gas has been subtracted from the gross buoyancy. Weights are in short tons (2,000 lb).

[c]80% ammonia decomposition.

[d]The cost of "Hypron C" includes processing and packaging into sealed cartridges (Proteus, Inc., Mountain Lakes, N. J.).

All the propellants listed in Table 15 are presently available in large quantities. Large quantity procurements might significantly reduce the price of the metal hydrides, but the other materials are already produced in such volume that large reductions seem unlikely.

DISPLACEMENT REQUIREMENTS

For ocean depths in excess of 1,000 ft, where the weight of the buoyant gas becomes important, comparisons of propellant cost on the basis of gross buoyancy (water displaced) is misleading. Figure 5 shows the net buoyancy per unit weight of water displaced as a function of ocean depth for the gas generating systems of the most interest. The practical

importance of these differences in net buoyancy is demonstrated in Fig. 6 where the relative displacement requirements (e.g., number or size of pontoons) for each system is shown as a bar graph (normalized to one for pure hydrogen).

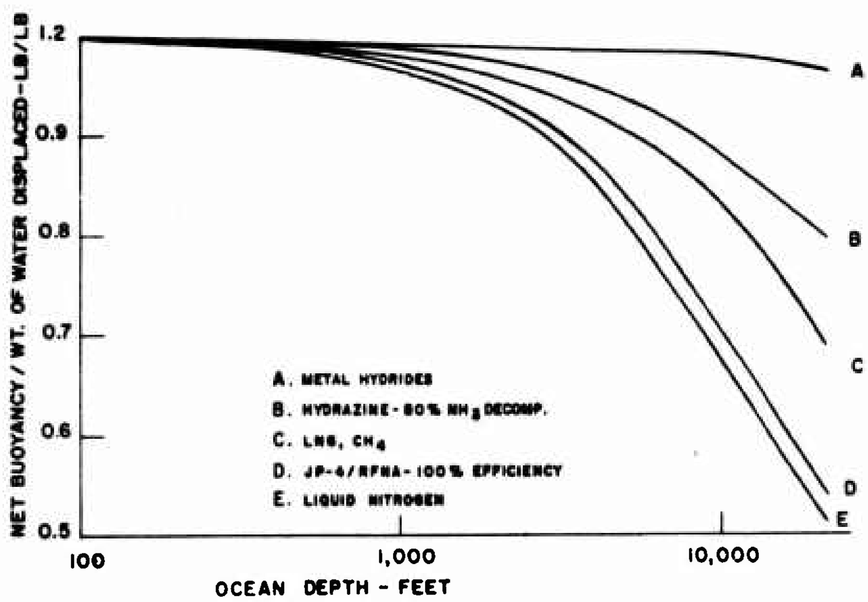

FIG. 5. Net Buoyancy of Gas Generating Reactions vs. Ocean Depth.

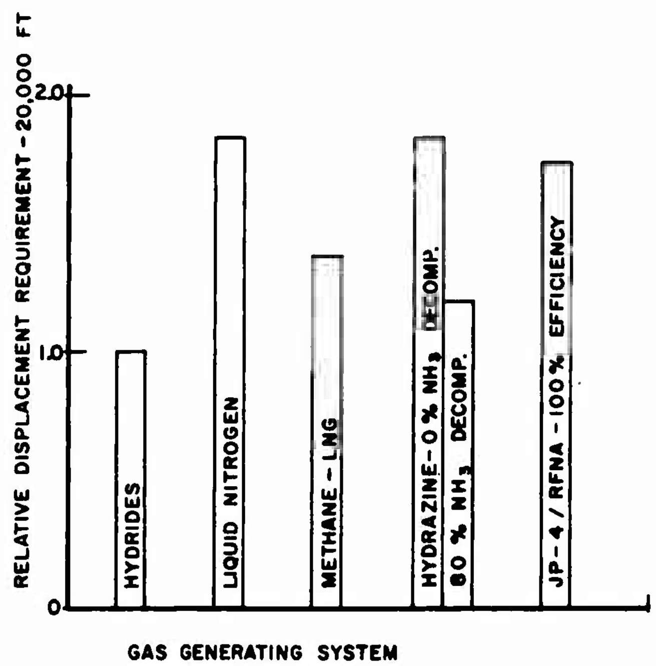

FIG. 6. Relative Displacement Requirements Using Product Gases for Various Gas Generating Propellants.

Obviously the propellant cost must be weighed against the expense of manufacturing, transporting, and deploying the number of pontoons required for lifting a given load.

STORAGE AND HANDLING

A summary of the storage, materials compatibility, toxicity, and flammability characteristics of the most promising gas generator propellants is given in Table 16. Liquid nitrogen, hydrogen and natural gas must be stored at cryogenic temperatures, but their low cost is a significant compensating factor for large lifts at moderate depths. Storage, handling, and safety problems are far greater for hydrogen than for nitrogen or natural gas. The other systems are all storable for acceptable time periods and are compatible with readily available materials.

Of the cryogenic liquids, LN_2 is to be preferred over LH_2 or LNG on the basis of flammability, but LNG has a large cost advantage, is less dense, and has a higher storage temperature. All are non-toxic.

Hydrazine is toxic while the metal hydrides are a problem only on direct contact, in which case the hydroxide formed from reaction with water is caustic. On the other hand, a hydrazine fire can be controlled with water while special dry chemicals are required for metal hydride fires.

Shipping regulations for these propellants are summarized in Table 17. A comprehensive discussion of these regulations can be found in Ref. 1.

CONCLUSIONS AND RECOMMENDATIONS

75 Tons at 12,000 and 20,000 Feet

The most significant advantages and disadvantages of the gas generating systems considered are listed in Table 18. Hydrazine and calcium hydride are the most economical chemical sources of buoyancy gases for the 12,000 and 20,000 ft missions consistent with acceptable buoyant efficiency and storage, handling, and safety considerations. Hydrazine has a cost advantage provided that a high reaction efficiency can be attained. This high efficiency is theoretically possible at high pressures, but quantitative experimental verification is lacking. A definitive study of the catalytic decomposition of hydrazine at pressures up to 9,000 psia is strongly recommended.

3,000 Tons at 850 Feet

At depths of less than 1,000 ft, where handling problems (pressure, deployment time, etc.) are reduced, cryogenic liquids offer a dramatic cost advantage over any conceivable chemical gas generator. Liquified natural gas is the lowest in cost, and hydrogen is the most efficient,

TABLE 16. Storage and Handling of Gas Generator Propellants

Propellant	Storage requirements	Compatible materials	Toxicity	Flammability
Hydrazine	Storable in sealed metal containers	Aluminum alloys, St. steel alloys, tantalum, titanium	Toxic	Moderate; vapor is detonable
Metalic sodium	Storable in containers, usually in hydrocarbon liquid	Compatible with most materials when free from moisture	Highly toxic if ingested; forms caustic NaOH with moisture	Highly flammable in presence of heat, moisture, oxidizers.
Lithium hydride	Storable in sealed containers	Compatible with most materials when dry; caustic when wet	Forms caustic LiOH with moisture	Highly flammable in the presence of heat or water; ignites in moist air
Calcium hydride	Storable in sealed containers	Compatible with most materials when dry, less caustic than LiH when wet	Forms caustic $Ca(OH)_2$ with moisture	Flammable in the presence of heat or water; difficult to ignite with moisture. Much more stable than LiH
Liquid hydrogen	Storable as a cryogenic liquid for limited periods	Non-reactive at normal storage and use temperatures	Non-toxic, a simple asphixiant	Very highly flammable
Liquid nitrogen	Storable as a cryogenic liquid for limited periods	Non-reactive at normal storage and use temperatures	Non-toxic, a simple asphixiant	Non-flammable

TABLE 16. (Contd.)

Propellant	Storage requirements	Compatible materials	Toxicity	Flammability
Liquid natural gas	Storable as a cryogenic liquid for limited periods	Non-reactive at normal storage and use temperatures	Non-toxic, a simple asphixiant	Highly flammable
JP-4	Ordinary tanks for petroleum products	Compatible with a wide range of metals and synthetic polymers	Harmful only in large concentrations	Flammable
Nitric acid (RFNA)	Storable in sealed metal containers	Aluminum alloys, stainless steel	Toxic	Very powerful oxidizing agent
Isopropyl nitrate	Storable in sealed metal containers	Stainless steel aluminum	No serious toxicity problems	Highly flammable

TABLE 17. Summary of Shipping Regulations for Gas Generator Propellants[a]

Propellant	Rail Express ICC[b]	Coast Guard classification	Air Freight IATA[c]
Hydrazine	Corrosive liquid white label, 5 pts	Corrosive liquid white label	Corrosive liquid, white label, 2-1/2 liter (cargo)
Metalic sodium	Flammable solid, yellow label, 25 lb	Inflammable solid, yellow label	Flammable solid, yellow label, not accepted (passenger) 12 kg (cargo)
Lithium hydride	Flammable solid, yellow label, 25 lb	Inflammable solid, yellow label	Flammable solid, yellow label, 12 kg (cargo)
Calcium hydride	See lithium hydride	See lithium hydride	See lithium hydride
Liquid hydrogen	Not accepted	Not permitted	Flammable gas, not accepted (passenger or cargo)
Liquid nitrogen	Non-flammable gas, green label, 300 lb	Non-inflammable gas, green gas label	Non-flammable gas, green label, 15 k (passenger and cargo)
Liquified natural gas (methane)	Flammable gas, red label, 300 lb	Inflammable gas, red label	Flammable gas, red label, 140 kg (cargo)
JP-4	....	....	....
Nitric acid	Corrosive liquid, white label, 5 pts	Corrosive liquid, white label	Corrosive liquid, white label, 2-1/2 liter (cargo)
Isopropyl nitrate	....	....	Flammable liquid, red label, 1 liter (passenger) 40 liters (cargo)

[a]Ref. 1 - Quantities listed refer to the maximum allowable in a single outside container.
[b]Interstate Commerce Commission.
[c]International Air Transport Association.

TABLE 18. Comparison of Gas Generator Propellants

Propellant	Major advantages	Major disadvantages
Hydrazine	Controllable reaction rate, moderate cost, possible high efficiency, fires and spills controllable with water	Toxic, flammable, uncertain efficiency at high pressure
Lithium hydride	High efficiency, low toxicity, low reaction temperature	High reactivity with heat or water, high cost, flammable, fire control requires special dry chemicals
Calcium hydride	Moderate efficiency, less reactive and more safely stored than LiH, low reaction temperature	Reactive with water or heat, high cost, flammable, fire control requires special dry chemicals
Liquid hydrogen	Low cost, high efficiency at all depths	Extremely low cryogenic storage temperature, high boil-off rate, very high explosion and fire hazard
Liquid natural gas (methane)	Very low cost, moderate efficiency down to 20,000 ft, highest storage temperature of useful cryogenic liquids	Cryogenic storage, flammable
Liquid nitrogen (air)	Low cost, non-toxic, non-flammable	Cryogenic storage, low efficiency (high density) at high pressure
JP-4/nitric acid	Low cost	Toxic, flammable, low efficiency at high pressure, actual performance unknown, large development cost
Lithium	Produces only hydrogen low reaction temperature	High cost, very reactive
Sodium	Produces only hydrogen, moderate cost, low reaction temperature	Very reactive, very low efficiency, high fire hazard

TABLE 18. (Contd.)

Propellant	Major advantages	Major disadvantages
Isopropyl nitrate	Moderate cost	Poor theoretical performances at high pressure, solid reaction products, uncertain and expected low reaction efficiency at high pressure
Solid propellants	Convenient storage	Low efficiency, high cost, poor control, particulates in products, exponential dependence of reaction rate on pressure (depth)

but nitrogen is chemically inert and, therefore, non-toxic and non-combustible. Problems associated with its very low storage temperature and high flammability render liquid hydrogen undesireable. The usefulness of cryogenic liquids will probably be limited by the depth to which they can be handled conveniently. An investigation into methods of applying these liquids to underwater buoyancy devices should be conducted.

Appendix A

THE CALCULATION OF BUOYANCY FACTORS

Pressure: The pressure at each depth was calculated assuming a constant seawater density of 64 lb/ft^3 (1.03 grams/cm^3). This assumption leads to the following expression for the absolute pressure (P) at any ocean depth (h):

$$P = 14.7 + 0.444h$$

where h is in units of feet and P is expressed in pounds per square inch. For example, at 20,000 ft

$$P = 14.7 + 0.444 \times 20{,}000 = 8902.7 \text{ psia}$$

Gas Volumes: The molar volume of each gas was calculated by the modified ideal gas law at an assumed temperature of 0°C,

$$V = \frac{ZRT}{P}$$

where: V is the volume of one mole of gas in liters

R is the ideal gas constant (0.08223 liter-atmospheres/mole)

T is the absolute temperature in degrees Kelvin

P is the pressure in atmospheres

Z is the "compressibility factor," an empirical quantity which allows for the non-ideality of the gas (see Appendix B)

For hydrogen at 20,000 ft and 0°C,

$$P = 8902.7 \text{ psia} = 605.63 \text{ atmospheres}$$

$$Z = 1.43$$

$$V = \frac{(1.43)(0.8223)(273.2)}{605.63} = 0.05305 \text{ liters}$$

BUOYANCY FACTOR (GASES)

The buoyancy factor is defined as the weight of water displaced (gross buoyancy) by a given weight of gas divided by the weight of the gas.

For hydrogen at 20,000 ft one gram-mole (2.016 grams) displaces 0.05305 liters of water (see above). This water weighs

$$0.05305 \text{ liters} \times 1.03 \times 10^3 \text{ grams/liter} = 54.64 \text{ grams}$$

Therefore the buoyancy factor for hydrogen at 20,000 ft is

$$54.64/2.016 = 27.10$$

BUOYANCY FACTOR (GAS GENERATOR PROPELLANTS)

The buoyancy factor for a gas generator propellant is defined as the weight of water displaced by the generated gas (gross buoyancy) divided by the weight of propellant required to generate the gas. For example, if hydrazine is catalytically decomposed and 80 percent of the resulting ammonia decomposes, the following product distribution is obtained.

$$3N_2H_4 \rightarrow 0.8NH_3 + 2.6N_2 + 4.8\ H_2$$

At 20,000 ft 3 moles of hydrazine (96.14 grams) produce 0.8 moles of ammonia, which is condensed and does not contribute to the lift, 2.6 moles of nitrogen, and 4.8 moles of hydrogen. The gas mixture displaces 415.23 grams of water, and the buoyancy factor for hydrazine is 415.23/96.14 = 4.32.

NET BUOYANCY

The net buoyancy is defined as:

$$\text{Net buoyancy} = \frac{\text{weight of water displaced} - \text{weight of buoyant gas}}{\text{weight of water displaced}}$$

For the hydrazine decomposition described above the weight of the buoyant gas is N_2 = 72.8 grams, H_2 = 9.6 grams, and the net buoyancy is

$$\frac{415.23 - (72.8 + 9.6)}{415.23} = 0.80$$

Appendix B

COMPRESSIBILITY FACTORS

The compressibility factor (Z) for a gas is defined as

$$Z = \frac{PV}{nRT}$$

where P is the pressure, V the volume, and T is temperature of n moles of gas at absolute temperature T. For an "ideal" gas Z = 1, but, at pressures above one atmosphere, Z may deviate appreciably from unity, and the ideal gas law leads to errors at up to 50 percent in buoyancy calculations for 20,000 ft ocean depths. The following compressibility factors were used in this report.

Compressibility Factors - 0°C

Gas	850 ft	12,000 ft	20,000	Reference
H_2	1.01	1.26	1.43	5,6
N_2	0.99	1.21	1.54	5,6
CO	0.99	1.18	1.56	7
CH_4	0.97	0.98	1.41	6,7
CO_2	0.85	....	....	6
Air	1.00	1.17	1.44	6

A comprehensive catalogue of compressibility factors and many other physical properties of industrial gases can be found in Ref. 6. For discussion purposes the compressibility factors of gases not shown above have been assumed to be the same as for hydrogen. This assumption does not lead to appreciable errors for the gases considered.

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13. ABSTRACT

Gases and gas generating materials have been reviewed to determine which are most suitable for ship salvage buoyancy devices. Three missions have been considered: a 3,000-ton lift from an ocean depth of 850 ft and 75-ton lifts from 12,000 and 20,000 ft. Hydrogen, nitrogen, oxygen, methane, ethane, and ethylene are the only gases suitable for these missions even at 850 ft. Hydrogen, nitrogen, oxygen, and methane are useful at 12,000 and 20,000 ft, also. Cryogenic liquids offer the most economical source of buoyancy gases, but their application to the deeper missions may be restricted by the high-pressure storage problems associated with their development. The catalytic decomposition of hydrazine and the calcium hydride-seawater reaction are the most promising gas generating chemical reactions. Since the performance of the hydrazine decomposition has not been studied quantitatively at the high pressures encountered in the 12,000 and 20,000 ft missions, such an investigation must be conducted before this system can be evaluated with confidence.

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